

English Abstract of Japanese Unexamined Patent Publication

No. 1994/175144

[Abstract]

[Title of the Invention] Ink precursor for forming a  
5 transparent, conducting film, and a method for forming a  
transparent, conducting ITO film

[Object] To provide an ink precursor that can  
greatly shorten the time necessary for conducting the  
entire process and can form transparent, conducting films  
10 with substantially high efficiency regardless of the size  
and type of substrate, and to provide a process for  
producing such a transparent, conducting ITO film.

[Constitution] An ink for forming a transparent,  
conducting ITO film comprising an organic In compound and  
15 an organic Sn compound containing one group selected from  
trimethyl, triethyl, tetramethyl and tetraethyl, both  
being dissolved in a hydrocarbon organic solvent. A  
method for forming a transparent, conducting ITO film, the  
method comprising printing a circuit on a substrate using  
20 the aforementioned ink, irradiating the substrate with  
ultraviolet radiation in air to simultaneously dissociate

the molecules of the hydrocarbon organic solvent, the organic In compound and organic Sn compound, and oxidize the In and Sn, thereby forming a transparent, conducting ITO film.

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(54)【発明の名称】 透明導電膜形成用インク前駆体及びITO透明導電膜形成方法

(57)【要約】

【目的】 基板の大きさ、種類に制限されず、また全工程に要する時間を大幅に短縮できて極めて高い効率で透明導電膜を形成することのできるインク前駆体及びITO透明導電膜形成方法を提供する。

【構成】 トリメチル、トリエチル、テトラメチル、テトラエチルのいずれかの有機Inと有機Snとが炭化水素系有機溶剤に混合されてなるITO透明導電膜形成用インク。上記インクを用いて基板に回路を印刷し、この回路基板に紫外線照射して炭化水素系有機溶剤、有機In、有機Snを解離させると同時に紫外線下大気中でIn、Snを酸化させてITO透明導電膜を形成することを特徴とするITO透明導電膜形成方法。

## 【特許請求の範囲】

【請求項1】 トリメチル、トリエチル、テトラメチル、テトラエチルのいずれかの基をもつ有機In及び／又は有機Snとが低沸点低分子量有機溶媒に混合されてなる透明導電膜形成用インク前駆体。

【請求項2】 トリメチル、トリエチル、テトラメチル、テトラエチルのいずれかの基をもつ有機In及び／又は有機Snとが炭化水素系有機溶剤に混合されてなる透明導電膜形成用インク前駆体。

【請求項3】 請求項1記載のITO透明導電膜形成用インクを用いて基板に回路を印刷し、この回路基板に紫外線照射して炭化水素系有機溶剤、有機In、有機Snを解離させると同時に紫外線下大気中でIn、Snを酸化させてITO透明導電膜を形成することを特徴とするITO透明導電膜形成方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、LCD、ELディスプレイ素子、エレクトロクロミック素子等の透明電極等に用いるITO透明導電膜を形成するのに用いるインク前駆体及びITO透明導電膜の形成方法に関する。

## 【0002】

【従来の技術】 従来よりITO薄膜を形成するには、CVD法（プラズマCVD法、光CVD法）やPVD法（蒸着、イオンプレーティング、スパッタリング）等がある。

【0003】 スパッタリング法を例にとって説明すると、材料として $\text{In}_2\text{O}_3$ 、 $\text{SnO}_2$ 、焼結ターゲットを用い、到達真空度  $5.0 \times 10^{-6}$  Torr、雰囲気純Ar  $5.0 \times 10^{-3}$  Torr、RF0.5kw程度、基板温度 400℃で成膜を行い、膜生成速度1000Å/minで抵抗率  $4.0 \times 10^{-4} \Omega \cdot \text{m}^2$  のITO膜を得ることができる。

【0004】 こうして成膜したITO膜で回路を形成するには、感光性レジストを用いてのフォトリソグラフィ工程（回路パターンニング）、ITOエッチング工程、レジスト剥離工程が必要となる。

【0005】 ところで、上記のようにITO膜の形成をパッチ式のスパッタリング装置で行なった場合、チャンバー容量の制限により基板の大きさ、枚数が制限される。またスパッター時、ITO膜の抵抗率を低下させる為に基板温度を上げる必要があり、またそれを上げなくとも電極での発熱により基板に対しダメージを与えることになる。従って、耐熱性の無い基板に対してはスパッターできず、基板の種類が限定せしめられる。さらに1パッチ当りのITO膜の形成に要する時間は60分程度であり、その後の回路形成に要する時間は60分以上であるので、効率が悪い。

【0006】 以上ITO膜の形成をスパッタリング法の場合について述べたが、蒸着法、イオンプレーティング法についても同様の問題点があり、プラズマCVD法、

光CVD法については成膜処理時間が非常に長くなるという問題点がある。

## 【0007】

【発明が解決しようとする課題】 そこで本発明は、基板の大きさ、種類に制限されず、低温で成膜でき、また成膜処理時間を短縮でき、さらには回路形成に要する時間も短縮できて効率良くITO透明導電膜を形成することのできるインク前駆体及びITO透明導電膜形成方法を提供しようとするものである。

## 【0008】

【課題を解決するための手段】 上記課題を解決するための本発明の透明導電膜形成用インク前駆体は、トリメチル、トリエチル、テトラメチル、テトラエチルのいずれかの有機In及び／又は有機Snとが低沸点低分子量の有機溶媒、とくに炭化水素系有機溶剤、たとえば、DMF、トルエン、ジブチルエーテル、ジフライム、メチルエチルケトン、メチルジクロヘキサノン、セロソルブアセテートなどに混合されてなるものである。

【0009】 また上記課題を解決するための本発明のITO透明導電膜形成方法は、上記構成のインク前駆体から形成されたインクを用いて基板に回路を印刷し、この回路基板に紫外線を低温（300℃以下、好ましくは100℃以下の温度）で照射して炭化水素系有機溶剤、有機In、有機Snを解離させると同時に紫外線下大気中でIn、Snを酸化させてITO透明導電膜を形成することを特徴とするものである。

## 【0010】

【作用】 上記のように本発明の透明導電膜形成用インク前駆体は、トリメチル、トリエチル、テトラメチル、テトラエチルのいずれかの基をもつ有機In及び／又は有機Snのアルキル化合物を素材としているので、非常に危険であるが有機溶媒によく溶解して取扱いが安全となる。そこで、紫外線で分解しやすい高沸点低分子量の有機溶媒を選択し、或る特定の波長より短い範囲にて解離され、またこれらの有機Inや有機Snの素材と混合している、特に炭化水素系有機溶剤も或る特定の波長より短い範囲にてただちに解離されるので、印刷技術により回路形成するのに極めて有効である。緻密な回路膜を形成しない場合には上記インク前駆体をそのままインクに使用することも可能である。

【0011】 また、本発明のITO透明導電膜形成方法は、上記インク前駆体から形成されたインクを用いて基板に回路を印刷するので、大型基板でも回路を印刷でき、またこの回路基板に紫外線を照射して炭化水素系有機溶剤、たとえば、DMF、トルエン、ジブチルエーテル、ジフライム、メチルエチルケトン、メチルジクロヘキサノン、セロソルブアセテートなど、有機In、有機Snを解離させると同時に紫外線下大気中でIn及びSnを酸化させてITO透明導電膜を形成するので、常溫処理となり基板は耐熱性のものに限定されることはな

い。しかも従来のCVD法やPVD法に比べ成膜処理時間、回路形成時間が短縮され、効率良くITO透明導電膜が得られる。なお、SnとInの酸化物の割合は5：95近辺が透明度が最も高く、低抵抗が得られ好ましい。

#### 【0012】

【実施例】本発明の透明導電膜形成用インク前駆体及びITO透明導電膜形成方法の一実施例を説明する。先ず、透明導電膜形成用インク前駆体について説明する。トリメチルIn（結晶）をトルエンに50wt%溶解した溶解液（インク前駆体A液）100gと、テトラメチルSn（液体）をトルエンに50wt%溶解した溶解液（インク前駆体B液）10gとを混合し、このA液とB液との混合液を100gの炭化水素系有機溶剤に混合し、この混合液をエバポレーターにてトルエンの分留を行い、重量100gとなった時点で分留を完了させ、炭化水素系有機溶剤にトリメチルIn及びテトラメチルSnが溶解したものをインク前駆体C液とした。必要に応じてこのC液を更に別の有機溶媒で分留したり、（このC液に粘度調整剤、増粘剤等を添加してインクとすることもでき、）またC液そのままでもインクとすることができる。

【0013】次にこのように合成したインク（C液）を用いるITO透明導電膜形成方法について説明する。一辺40mmの方形のPETフィルムを基板としてこの上に、回路が形成された版を用いて上記インクを2mm厚に印刷した。次にこの回路を印刷した基板に対し、水銀ランプ（200～400nm）にて紫外線照射を室温にて3分間行い、炭化水素系有機溶剤の解離を開始し、引き続き紫外線照射により発生したオゾン雰囲気中で重水素ランプ（115nm）にて紫外線照射を5分間行い、炭化水素系有機溶剤、トリメチルIn、テトラメチルSnを解離させると同時にオゾンによりIn、Snを酸化させて $\text{In}_2\text{O}_3$ 、 $\text{SnO}_2$ を形成し、ITO透明導電膜を得た。

【0014】こうして得たITO透明導電膜をガスクロマトフィで分析した処、メチル基が検出され、紫外線照射によりトリメチルIn、テトラメチルSnが分解されたことが確認できた。

【0015】上記のITO透明導電膜形成方法では、インクを合成するのに30分かかったが、その後の印刷、膜形成に要する時間は室温で20分程度であったので、従来のCVD法やPVD法によるITO透明導電膜の形成時

間に比べれば半分以下であり、必要量のインクを合成してしまえば処理時間は1回当たり20分程度で良いので、極めて高い効率でITO透明導電膜が得られることになる。

【0016】尚、透明導電膜形成用インク前駆体は、上記実施例の手順で合成する方法に限定されるものではなく、次のような手順で合成する方法もある。炭化水素系有機溶剤100gに、トリメチルIn（結晶）をトルエンに50wt%溶解した溶解液100gを混合し、この混合液をエバポレーターにてトルエンの分留を行い、重量100gとなった時点で分留を完了させ、この混合液100gにテトラメチルSn（液体）をトルエンに50wt%溶解させた溶解液10gを混合し、この混合液をエバポレーターにてトルエンの分留を行い、重量100gとなった時点で分留を完了させ、炭化水素系有機溶剤にトリメチルIn、テトラメチルSnが溶解したものをインク前駆体とした。

【0017】また上記実施例のインクは、素材の有機InがトリメチルInでもあるが、トリエチルIn、テトラメチルIn、テトラエチルInでも良いものであり、有機SnはテトラメチルSnに代えてテトラエチルSn、トリメチルSn、トリエチルSnでも良いものである。

#### 【0018】

【発明の効果】以上の説明で判るように本発明の透明導電膜形成用インク前駆体は、有機In及び／又は有機Snのアルキル化合物を素材とし、またこれらの素材を炭化水素系有機溶剤と混合したものであるから紫外線照射により解離でき、従って印刷技術により回路形成するのに極めて有効である。

【0019】また本発明のITO透明導電膜形成方法は、上記インクを用いて印刷法により基板に回路を形成するので、基板の大きさに限定されることはなく、またこの回路基板に紫外線照射して炭化水素系有機溶剤、有機In、有機Snを解離させると同時に紫外線下大気中でIn、Snを酸化させてITO透明導電膜を形成するので、常温処理となり、基板は耐熱性のものに限定されることがない。しかも従来のCVD法やPVD法に比べ全工程に要する時間が著しく短縮され、ITO透明導電膜を極めて高い効率で得ることができる。

PATENT ABSTRACTS OF JAPAN

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(54) INK PRECURSOR FOR FORMATION OF TRANSPARENT CONDUCTIVE FILM  
AND FORMING METHOD OF ITO TRANSPARENT CONDUCTIVE FILM  
.....

(57)Abstract:

PURPOSE: To provide an ink precursor and a method to form an ITO transparent conductive film so that a transparent conductive film can be formed at high efficiency and the time necessary for the whole process can be largely decreased without depending the size and kind of substrates.

CONSTITUTION: This ink to form an ITO transparent conductive film is obtd. by mixing org. In and org. Sn selected from trimethyl-, triethyl-, tetramethyl-, and tetraethyl-In and Sn in a hydrocarbon org. solvent. This ink is used to print a circuit on a substrate. The substrate is then irradiated with UV rays to dissociate the hydrocarbon org. solvent, org. In, and org. Sn. At same time, In and Sn are oxidized in air with irradiation of UV rays to form an ITO transparent conductive film.  
.....

→ no halogen  
= halogen  
(?)

[Claim(s)]

[Claim 1] organic [ with the basis of triethyl, trimethyl, tetramethyl one, or tetraethyl ]  
-- the ink precursor for transparent electric conduction film formation with which a  
low-boiling point low-molecular-weight organic solvent comes to mix In and/or organic  
[ Sn ]

[Claim 2] organic [ with the basis of trimethyl, triethyl, tetramethyl one, or tetraethyl ]  
-- the ink precursor for transparent electric conduction film formation with which the  
hydrocarbon system organic solvent comes to mix In and/or organic [ Sn ]

[Claim 3] the ink for ITO transparent electric conduction film formation according to  
claim 1 -- using -- a substrate -- a circuit -- printing -- this circuit board -- UV irradiation  
-- carrying out -- the hydrocarbon system organic solvent and organic -- the ITO  
transparent electric conduction film formation method characterized by oxidizing In  
and Sn in the bottom atmosphere of ultraviolet rays, and forming an ITO transparent  
electric conduction film at the same time it makes In and organic [ Sn ] dissociate  
DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the formation method of the ink  
precursor used for forming the ITO transparent electric conduction film used for  
transparent electrodes, such as LCD, an ElectroLuminescent Display element, and an  
electrochromic element, etc., and an ITO transparent electric conduction film.

[0002]

[Description of the Prior Art] In order to form an ITO thin film conventionally, there are  
CVD (a plasma CVD method, optical CVD), PVD (vacuum evaporatio~~no~~, ion plating,  
sputtering), etc.

[0003] When it explains taking the case of the sputtering method, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and a  
sintering target are used as a material, and it is ultimate vacuum.  $5.0 \times 10^{-6}$  Torr,  
atmosphere pure Ar  $5.0 \times 10^{-3}$  Torr, about RF0.5kw, substrate temperature Membranes  
are formed at 400 degrees C and they are 1000A of film generation rates, and min.  
Resistivity  $4.0 \times 10^{-4}$  ohm·m 2 An ITO film can be obtained.

[0004] In this way, in order to form a circuit by the ITO film which formed membranes,  
the photo lithography process using a photosensitive resist (circuit patterning), an ITO  
etching process, and a resist ablation process are needed.

[0005] By the way, when an ITO film is formed by the sputtering system of a batch type  
as mentioned above, the size of a substrate and number of sheets are restricted by limit  
of chamber capacity. Moreover, at the time of a spatter, in order to reduce the resistivity  
of an ITO film, even if it is necessary to raise substrate temperature and and does not  
raise it, a damage will be given to a substrate by generation of heat by the electrode.  
Therefore, a spatter cannot be carried out to a substrate without thermal resistance, but

the kind of substrate is made to limit. Since the time which formation of the ITO film per further 1 batch takes is about 60 minutes and the time which subsequent circuit formation takes is 60 minutes or more, efficiency is bad.

[0006] Although formation of an ITO film was described about the case of the sputtering method above, there is a trouble with the same said of a vacuum deposition and the ion plating method, and there is a trouble that the membrane formation processing time starts very long, about a plasma CVD method and optical CVD.

[0007]

[Problem(s) to be Solved by the Invention] Then, it is going to offer the ink precursor and the ITO transparent electric conduction film formation method of this invention not being restricted to the size of a substrate, and a kind, being formed at low temperature, and being able to shorten the membrane formation processing time, also shortening the time which circuit formation takes further, and forming an ITO transparent electric conduction film efficiently.

[0008]

[Means for Solving the Problem] the ink precursor for transparent electric conduction film formation of this invention for solving the above-mentioned technical problem -- organic [ of trimethyls, triethyl, tetramethyl one, or tetraethyl ] -- organic solvent [ of low-boiling point low molecular weight ] especially hydrocarbon system organic solvent, for example, DMF, toluene, dibutyl ether, diglyme, methyl-ethyl-ketone, and methyl cyclohexanon, a cellosolve acetate etc. comes to mix In and/or organic [ Sn ]

[0009] Moreover, the ITO transparent electric conduction film formation method of this invention for solving the above-mentioned technical problem A circuit is printed to a substrate using the ink formed from the ink precursor of the above-mentioned composition. this circuit board -- ultraviolet rays -- low temperature (300 degrees C or less, preferably temperature of 100 degrees C or less) -- irradiating -- the hydrocarbon system organic solvent and organic -- it is characterized by oxidizing In and Sn in the bottom atmosphere of ultraviolet rays, and forming an ITO transparent electric conduction film at the same time it makes In and organic [ Sn ] dissociate

[0010]

[Function] organic [ in which the ink precursor for transparent electric conduction film formation of this invention has the basis of trimethyl, triethyl tetramethyl one, or tetraethyl as mentioned above ] -- since it is made from In and/or the alkyl compound organic [ Sn ], although it is very dangerous, it dissolves in an organic solvent well and handling becomes safe Then, since especially the hydrocarbon system organic solvent is also immediately dissociated in the range shorter than a certain specific wavelength which the organic solvent of the high-boiling point low molecular weight which is easy to decompose by ultraviolet rays is chosen, and dissociates in the range shorter than a certain specific wavelength, and is mixed with these organic In(s) and materials organic [ Sn ], it is very effective in carrying out circuit formation with printing technology.

When not forming a precise circuit film, it is also possible to use the above-mentioned ink precursor for ink as it is.

[0011] Moreover, the ITO transparent electric conduction film formation method of this invention is since a circuit is printed to a substrate using the ink formed from the above-mentioned ink precursor. a large-sized substrate -- a circuit -- it can print -- moreover, this circuit board -- ultraviolet rays -- irradiating -- organic [ , such as hydrocarbon system organic solvent, for example, DMF, toluene dibutyl ether, diglyme, methyl-ethyl-ketone, and methyl cyclohexanon and a cellosolve acetate, ] -- since In and Sn are oxidized in the bottom atmosphere of ultraviolet rays and an ITO transparent electric conduction film is formed at the same time it makes In and organic [ Sn ] dissociate, it becomes ordinary temperature processing and a substrate is not limited to a heat-resistant thing And compared with conventional CVD and conventional PVD, the membrane formation processing time and circuit formation time are shortened, and an ITO transparent electric conduction film is obtained efficiently. In addition, the 5:95 neighborhoods are the highly transparent, low resistance is obtained and the rate of the oxide of Sn and In is desirable.

[0012]

[Example] One example of the ink precursor for transparent electric conduction film formation of this invention and the ITO transparent electric conduction film formation method is explained. First, the ink precursor for transparent electric conduction film formation is explained. trimethyl In (crystal) -- toluene -- 50wt(s)% -- dissolved solution (ink precursor A liquid) 100 g, 10g (ink precursor B liquid) of dissolved solutions is mixed. tetramethyl one Sn (liquid) -- toluene -- 50wt(s)% -- Mixed liquor of this A liquid and B liquid It mixes to the 100g hydrocarbon system organic solvent. this mixed liquor -- an evaporator -- fractional distillation of toluene -- carrying out -- weight fractional distillation is completed when set to 100g -- making -- the hydrocarbon system organic solvent -- trimethyl one -- what In and tetramethyl one Sn dissolved was used as ink precursor C liquid the need -- responding -- distilling this C liquid fractionally by still more nearly another organic solvent \*\*\*\* -- again (being able to add a viscosity controlling agent, an adding a-car-to-a-train agent, etc. in this C liquid, and also being able to consider as ink) -- C liquid -- even if it remains as it is, it can consider as ink

[0013] Next, the ITO transparent electric conduction film formation method using the ink (C liquid) compounded in this way is explained. The above-mentioned ink was printed to 2mm \*\* using the version with which the circuit was formed on this by using the PET film of an one-side a 40mm rectangle as a substrate. Next, to the substrate which printed this circuit, a room temperature performs UV irradiation for 3 minutes in a mercury lamp (200 to 400 mm), the maceration of the hydrocarbon system organic solvent is started, and it is UV irradiation succeedingly. the inside of the generated ozone atmosphere -- deuterium lamp (115mm) UV irradiation -- for 5 minutes -- carrying out -- the hydrocarbon system organic solvent and trimethyl one -- while

making In and tetramethyl one Sn dissociate, In and Sn were oxidized by ozone, In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> were formed, and the ITO transparent electric conduction film was obtained [0014] in this way, the place and methyl group which analyzed the obtained ITO transparent electric conduction film by gas chromatography TOFMS detect -- having -- UV irradiation -- trimethyl one -- it has been checked that In and tetramethyl one Sn had been decomposed

[0015] Although it took 30 minutes by the above-mentioned ITO transparent electric conduction film formation method to compound ink, since the time which subsequent printing and film formation take was about 20 minutes at the room temperature. If compared with the formation time of the ITO transparent electric conduction film by conventional CVD and conventional PVD, it will be below a half, and if the ink of an initial complement is compounded, since it is good, as for the processing time, an ITO transparent electric conduction film will be obtained at very high efficiency in about 20 minutes per time.

[0016] In addition, the ink precursor for transparent electric conduction film formation is not limited to the method of compounding in the procedure of the above-mentioned example, and also has the method of compounding in the following procedures. hydrocarbon system organic solvent 100g -- trimethyl one -- In (crystal) Mix 100g of dissolved solutions and toluene is distilled fractionally for this mixed liquor in an evaporator. toluene -- 50wt(s)% -- fractional distillation is completed when it becomes the weight of 100g -- making -- this mixed liquor 10g of solutions in which it was made to dissolve is mixed. 100g -- tetramethyl one Sn (liquid) -- toluene -- 50wt(s)% -- this mixed liquor -- an evaporator -- fractional distillation of toluene -- carrying out -- weight fractional distillation is completed when set to 100g -- making -- the hydrocarbon system organic solvent -- trimethyl one -- In and the thing which tetramethyl one Sn dissolved were used as the ink precursor

[0017] moreover, the ink of the above-mentioned example -- organic [ of a material ] -- In -- trimethyl one -- although it is also In, Triethyl In, tetramethyl one In, and Tetraethyl In are sufficient, and Tetraethyl Sn, trimethyl one Sn, and Triethyl Sn are [ organic / Sn / may be replaced with tetramethyl one Sn and ] sufficient as it

[0018]

[Effect of the Invention] it understands by the above explanation -- as -- the ink precursor for transparent electric conduction film formation of this invention -- organic -- it is very effective in being able to dissociate by UV irradiation, since it is made from In and/or an alkyl compound organic [ Sn ] and these materials are mixed with the hydrocarbon system organic solvent, therefore carrying out circuit formation with printing technology

[0019] Moreover, the ITO transparent electric conduction film formation method of this invention is since a circuit is formed in a substrate by print processes using the above-mentioned ink. being limited to the size of a substrate -- there is nothing -- moreover,

this circuit board -- UV irradiation -- carrying out -- the hydrocarbon system organic solvent and organic -- since In and Sn are oxidized in the bottom atmosphere of ultraviolet rays and an ITO transparent electric conduction film is formed at the same time it makes In and organic [ Sn ] dissociate, it becomes ordinary temperature processing and a substrate is not limited to a heat-resistant thing And the time which all processes take compared with conventional CVD and conventional PVD is shortened remarkably, and an ITO transparent electric conduction film can be obtained at very high efficiency.